

Physical and Chemical Properties Division (838)

Richard F. Kayser, Chief

A. Overview

Mission

The Physical and Chemical Properties Division is the Nation's reference laboratory for measurements, standards, data, and models for:

- the thermophysical and thermochemical properties of gases, liquids, and solids – both pure materials and mixtures
- the rates and mechanisms of chemical reactions in the gas and liquid phases
- fluid-based physical processes and systems, including separations, low-temperature refrigeration, and low-temperature heat transfer and flow.

The Division provides technical research and services, Standard Reference Data, Standard Reference Materials, and calibrations to promote U.S. economic growth and to assist U.S. industry, other government agencies, and academia in solving problems of national importance.

Functions

In the areas of thermophysics, thermochemistry, and kinetics, the Division

- develops, maintains, and uses state-of-the-art apparatus to perform experimental measurements on industrially and scientifically important systems
- compiles, evaluates, and correlates experimental data
- develops and evaluates state-of-the-art theories, models, estimation methods, and computational approaches
- disseminates results by a wide variety of mechanisms

In the area of cryogenic technologies, the Division provides engineering data, models, and research to support the development of advanced cryocoolers, and measurement methods, standards, and services for flow under cryogenic conditions.

Current Focus Areas

Current focus areas include *Basic Reference Data and Computational Techniques*, *Data for Process and Product Design*, *Properties of Energy-Related*

Fluids, *Environmental Fates of Industrial Chemicals*, *Tools for Chemical Analysis*, *Fundamental Studies of Fluids*, and *Cryogenic Technologies*. Brief descriptions of these areas follow, with references to selected Technical Highlights (see next section).

Basic Reference Data and Computational Techniques

Physical, chemical, and kinetic data and models are important in research and development, process modeling, process design, energy efficiency, safety, health, transportation and storage, custody transfer, and the environment. Scientists and engineers require sufficient data for many substances to determine parameters in commonly used models, to develop new and improved estimation methods and models, and to evaluate and intercompare estimation methods, models, and computational techniques. The principal components of this program are:

- to compile, evaluate, and disseminate data and predictive methods for chemical species and systems of broad interest to a large number of diverse users
- to develop, apply, and assess computational approaches for acquiring such data

During 1997, the Division initiated a new program in quantum chemistry focused on developing resources to aid industrial scientists and engineers in the computation of molecular properties. These resources will include:

- critical comparisons of computational results with the best available experimental data,
- interactive guidance for the non-expert on methods, reliability, and resource requirements,
- a searchable repository where scientists may submit or extract the results of standard calculations

For additional information on *Basic Reference Data and Computational Techniques*, see Technical Highlights 1-6 and 31.

Data for Process and Product Design

Process and product design in a wide variety of industries depends on the availability of high-quality physical and chemical properties data and models. The availability of such information has played a key role in the emergence of process simulators as a key enabling technology in the chemical and related industries. Large-scale process modeling and simulation is also growing in importance in areas such as semiconductor processing and the treatment of hazardous wastes. The Division's goal is to provide the underlying data and models needed to support such developments. Areas of current interest include:

- semiconductor processing
- chemical and materials processing
- separations
- advanced oxidation technologies
- combustion

For additional information, see Technical Highlights 7-12.

Properties of Energy-Related Fluids

Industry requires accurate and comprehensive equilibrium and transport properties data and models for energy-related fluids in several key areas, including the design and optimization of working cycles in refrigeration systems and power plants; the design, control, and optimization of gas processes; and custody transfer. Efforts in this area include the development of experimental apparatus, the acquisition of needed data, and the development and dissemination of high-accuracy correlations. Fluids under study include:

- alternatives to ozone-depleting chlorofluorocarbons and hydrochlorofluorocarbons for use in air-conditioning and refrigeration systems
- alternatives to steam for use in power cycles, e.g., ammonia-water mixtures
- noble gas mixtures for use in thermoacoustic refrigerators
- natural gas systems

During 1997, the Division developed plans to expand its experimental and modeling research on the properties of natural gas systems. Major goals of the program are to develop the means to accurately model and predict the thermodynamic, phase equilibrium, and transport properties of natural gas, liquefied natural gas (LNG), natural gas liquids (NGLs), substitute/synthetic natural gas (SNG), compressed natural gas (CNG), and wet, dry, and sour gases. For additional information on

Properties of Energy-Related Fluids, see Technical Highlights 13-16.

Environmental Fates of Industrial Chemicals

A wide variety of physical, chemical, interfacial, and kinetic data and data prediction methods are essential to understand and assess the long-term fates of new and existing chemicals in the atmosphere and in ground water. Properties of interest include atmospheric lifetimes, aqueous solubilities, ion-exchange equilibria, and partition coefficients. Current efforts are focusing on:

- the atmospheric chemistry and lifetimes of alternative refrigerants, alternative fire suppressants, and oxygenated fuel additives
- the thermodynamics and kinetics of selected species in aqueous solution.

During 1997, the Division initiated a multi-year program on thermodynamic properties for environmental fate and risk analysis, with the principal emphasis on heavy-metal-containing species and the common ions with which these species come into contact in aqueous environments. This program will comprise:

- an assessment and analysis of the state of the literature regarding selected species and properties
- the development of needed experimental capabilities
- the acquisition of experimental data to fill gaps and resolve discrepancies in the data
- the development of comprehensive models for the thermodynamic properties of "key substances"
- the construction of a data-handling system to manage the resulting network of thermodynamic information in a thermodynamically consistent manner.

For additional information, see Technical Highlights 17-18.

Tools for Chemical Analysis

The analysis of simple and complex mixtures and the identification of individual chemicals are tasks central to many aspects of the chemical and related industries, including research and development, production, and quality assurance and control. These tasks are also crucial in environmental monitoring, medical research, and health care. In this area, the Division strives to produce critically evaluated data, predictive models, and software to assist in the analysis and identification of as wide a

range of species as possible. Areas of current emphasis include:

- mass spectral (MS) data and databases
- gas chromatographic (GC) data and databases
- infrared data and databases
- tools for automatically deconvoluting and analyzing GC/MS data files

In the latter area, the Division is working with the U.S. Defense Special Weapons Agency, the Organization for the Prevention of Chemical Weapons, and others to develop software for use in on-site inspections under the Chemical Weapons Convention. For additional information, see Technical Highlights 19-20.

Fundamental Studies of Fluids

The goals of this program are to develop and use unique experimental, theoretical, and simulational capabilities to study fluid systems under equilibrium and non-equilibrium conditions, with and without chemical reactions. Topics under investigation include:

- the effects of shear on the microscopic structure of colloids, gels, micelles, and emulsions and on the dynamics of processes such as coagulation, gelation, and association
- the behavior of the viscosity of a pure fluid very close to its critical point in microgravity
- hydrogen bonding in water and related systems
- fluid-solid phase transitions
- new primary standards for temperature and pressure.

For additional information, see Technical Highlights 21-26.

Cryogenic Technologies

Cryogenic technologies such as pulse-tube refrigerators underpin a wide variety of technically important areas. These areas include the cooling of electronics for high-speed computing and communications, the production of ultra-clean environments for semiconductor processing, the liquefaction of natural gas from remote gas wells and for use as a clean fuel, the cooling of medical instruments, and the cooling of satellite-based infrared sensors for military and environmental applications. Research in this program addresses all of these topics, with the primary focus on:

- the development of improved measurement and modeling techniques for characterizing basic

cryocooler components and processes in the temperature range from 120 K to below 10 K

- collaborations with industry and others to support the development of cryocoolers for specific applications
- the measurement of cryogenic flows.

During 1997, the Division initiated a new program in microscale heat transfer. The goal is to develop and validate models and correlations for predicting heat transfer between fluids and solids when the length or time scale over which the heat transfer takes place becomes very small. For additional information, see Technical Highlights 27-28.

Selected Technical Accomplishments

- release of two major upgrades of the NIST Chemistry WebBook (see Technical Highlight 1)
- publication of evaluated proton affinity database and primary scale based on data for 1700+ species (2)
- new facility for measuring the thermophysical properties of gases used in semiconductor processing (7)
- revision of refrigerant properties in the 1997 ASHRAE Handbook of Fundamentals (13)
- measurement of retention parameters of selected hydrocarbons on selected stationary phases and incorporation of results into the database used by the natural gas industry to analyze the C₆+ fraction of natural gas (15)
- completion of adiabatic twin-cell calorimeter for performing high-accuracy measurements of isochoric heat capacity of compressed gases and liquids (16)
- first-ever demonstration of the use of cavity-ring-down technology for studying transient phenomena in condensed phases (18)
- measurement of the viscosity of xenon near its critical point with state-of-the-art accuracy in a microgravity environment (23)
- use of molecular dynamics to delineate different regimes of hydrogen bonding in water over wide ranges of conditions (24)
- acquisition of comprehensive data on the thermal conductances of stacked screens for optimizing the design of regenerative heat exchangers (27)

Selected Conferences and Workshops

Major international conferences:

- Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, CO (Technical Highlight 29)
- Fourth International Conference on Chemical Kinetics, July 14-18, 1997, Gaithersburg, MD (Technical Highlight 30)

Topical meetings:

- DIPPR Liaison Forum, November 11, 1996, Chicago, IL
- Special Topics in Statistical Mechanics – A Symposium in Honor of Raymond D. Mountain, April 10-11, 1997, Gaithersburg, MD
- Meeting of International Energy Agency Annex 18 on the Thermophysical Properties of the Alternative Refrigerants, June 20, 1997, Boulder, CO
- Meeting of IUPAC Subcommittee on Transport Properties, June 21-22, 1997, Boulder, CO

Organizational Structure

The Physical and Chemical Properties Division has research groups in Gaithersburg, Maryland and Boulder, Colorado, with the equivalent of 35-40 full-time staff in each location. Dr. William M. Haynes directs the Boulder part of the Division. The structure and technical activities of the Division are as follows:

Division-Office Programs (Gaithersburg and Boulder)

- study the behavior of fluid systems under both equilibrium and non-equilibrium conditions using unique experimental, theoretical, and simulational capabilities

Process Separations Group (Boulder)

- performs basic and applied research on a variety of separation processes, including distillation, supercritical fluid extraction, adsorption, and membrane separations
- provides critically-evaluated data and models needed to design and/or select more efficient and robust separation processes

Fluid Science Group (Gaithersburg)

- develops and applies state-of-the-art techniques based on acoustics and other novel approaches for measuring the thermodynamic and transport properties of fluids and fluid mixtures, including refrigerants and semiconductor processing gases

- performs research on next-generation primary standards in the areas of temperature, pressure, and low flow rate

Experimental Kinetics and Thermodynamics Group (Gaithersburg)

- develops and uses state-of-the-art measurement techniques to determine the rates and mechanisms of chemical reactions in the gas and liquid phases and the thermodynamic properties of industrially and environmentally important chemical species and materials
- develops new measurement methods for detecting and characterizing reactive intermediates
- certifies Standard Reference Materials for thermodynamic properties important to industry and science

Chemical Reference Data and Modeling Group (Gaithersburg)

- develops and evaluates new theories, models, estimation methods, and computational techniques for thermodynamic properties and rate constants
- compiles, evaluates, correlates, and disseminates Standard Reference Data
- develops and disseminates electronic databases and software on thermodynamics, chemical kinetics, and analytical mass and infrared spectra

Experimental Properties of Fluids Group (Boulder)

- performs experimental research and develops and maintains high-accuracy apparatus for measuring the full complement of thermodynamic and transport properties of fluids and fluid mixtures over wide ranges of temperature, pressure, and composition
- provides comprehensive thermophysical property measurements for technically important pure fluids and mixtures, including common organics and inorganics, hydrocarbons, refrigerants, and aqueous systems

Theory and Modeling of Fluids Group (Boulder)

- performs theoretical and simulational research on the thermophysical properties of fluids and fluid mixtures, including regions of fluid-fluid and fluid-solid phase separation
- develops models and correlations of high accuracy to describe and predict the thermophysical properties of fluids and fluid mixtures
- provides comprehensive and evaluated Standard Reference Data and electronic databases for the properties of technically important fluids and fluid mixtures

Cryogenic Technologies Group (Boulder)

- develops improved measurement and modeling techniques for characterizing basic cryocooler components and processes
- develops state-of-the-art cryocoolers for specific applications
- provides measurement methods, standards, and services for flow under cryogenic conditions

Staff Recognition for Fiscal Year 1996

- Richard F. Kayser, Senior Executive Service Presidential Rank Award for Meritorious Service
- Jan V. Sengers, Election to Fellow of the American Society of Mechanical Engineers for outstanding contributions to the field of thermophysical properties of fluids and fluid mixtures

B. Selected Technical Reports

1. *The NIST WebBook - NIST Chemical Reference Data for Industry*

W.G. Mallard, P.J. Linstrom, J.F. Liebman (UMBC), H. Affey (UMBC), and P.J. Christian

Objective: To provide Internet access to a complete set of chemical data with a common interface that provides both ease of use and a simple method to expand as more data become available.

Problem: There is an enormous amount of organic thermochemical data (heats of formation, entropies, heat capacities, heats of reaction) that are largely unknown to the technical community. One part of this project is to find and evaluate those data. In addition, there is a need to make available ancillary thermochemical data such as phase-change enthalpies. Data on infrared (IR) spectra, mass spectra, and other analytical techniques are also important resources that are often difficult to find. For all of the data it is essential that tools be provided to make the data easy to access.

Approach: The rapid growth of the World Wide Web has been widely remarked upon. The most enthusiastic appraisal of the future of the Web is unrealistic, but it is clear that the Web has dramatically changed the way that science is done. The use of the Web as a publishing medium and as a resource for communication has been growing rapidly. What has not followed is the development of data resources for the Web. The WebBook is an effort to correct this. The WebBook will provide a quick and direct source of data available at all times. The initial efforts are tied to an approach based on compounds rather than properties. All the data on benzene, for example, are gathered together, rather than all the data on heat of combustion. While the major thrust of the WebBook is to supply data from NIST evaluations, the role of the WebBook in providing a resource for chemical data from all sources will expand. In parallel with the efforts to gather and evaluate data, another major part of this project is aimed at providing the mechanisms needed to make these and other NIST chemical reference

data available on the Internet. These efforts are part of NIST's program on Systems Integration for Manufacturing Applications (SIMA).

Results and Future Plans: During FY97, the second and third editions of the NIST Chemistry WebBook* were released. The original data set, which included a number of estimated values, was edited to include only experimental data. The total number of compounds for which data was provided more than doubled in the second release (from 11,000 to 22,300 compounds) and was further increased in the third release (to 27,300 compounds). In addition, a number of new types of data were added. In the second release, data were added on vapor pressure, infrared spectra, and mass spectra. Data for vapor pressure as a function of temperature were added for over 1500 compounds in the form of Antoine coefficients. In addition, far more extensive data were provided for phase-transition enthalpy, including data for the temperature dependence of the enthalpy for a selected set of compounds. The third release included high accuracy thermophysical properties data for thirteen important industrial fluids. For these fluids, the WebBook allows the user to calculate selected properties along an isotherm, an isobar, or the saturation line (as either a function of temperature or pressure). In addition, an extensive set of data was added on negative ion energetics. The WebBook has been extremely well received, as demonstrated by the number and variety of users from industry, government, and academia. Both the number of users (5000 per week) and the number of repeat users (1800 per week) have continued to grow steadily. The WebBook is also a tool to aid future evaluation projects, both at NIST and in collaborations with others. A long-term goal is to provide a single point of entry for access to all chemical data at NIST.

*<http://WebBook.nist.gov>

2. *Evaluated Proton Affinity Database*

E.P. Hunter and S.G. Lias

Objective: To develop an evaluated proton affinity database for use in determining the thermochemistry of ions and ionic clusters.

Problem: The energy associated with ionizing a molecule can sometimes be determined to very high accuracy. However, for the majority of molecules, especially radicals, this is difficult at best.

Approach: Rather than measuring the enthalpy of formation of ionic species, it is generally easier to measure the difference between the energy of one species and another. The resulting energy differences can be formed into a thermochemical "ladder". Absolute thermochemical values can then be obtained by referring all of these differences, either directly or indirectly, to a relatively small number of molecules that together constitute a primary thermochemical scale. Great care is taken to ensure that the thermochemical values assigned to these primary molecules are consistent with absolute values that have been determined for the individual molecules and with differences that have been determined for pairs of molecules.

Results and Future Plans: The data from 1700+ compounds contained in 500+ references have been analyzed and evaluated. Discrepancies have been identified and, where possible, resolved. For the first time it has been possible to rely on some computational results to resolve experimental uncertainties. While in principal the experimental data are simple, in practice the level of detail needed to understand which of the multiple experiments are correct has meant that this work was a far more extensive undertaking than originally envisioned.

The results of the work have been submitted for publication in the Journal of Physical and Chemical Reference Data. In addition, they have been made available in the NIST WebBook (see Technical Highlight 1). It is anticipated that the use of this electronic medium will allow rapid feedback on any remaining points of controversy. Evaluations such as this are important in providing useful points of reference for future work. By providing all of the data in a single source and pointing out the

remaining areas of disagreement, they allow for a refocusing of experimental and theoretical efforts.

The role of computation in the future of ion energetics has also been clearly established by this work. The computational results were essential in the effort to develop a consistent set of values that could be used as a primary scale. Future work will require that larger scale computations be attempted to establish reference values for larger molecules.

Publication:

Hunter, E.P.L. and Lias, S.G., "**Evaluated Gas Phase Basicities and Proton Affinities of Molecules: An Update,**" J. Phys. Chem. Ref. Data (in press).

3. *Reference Thermodynamic Formulations for Pure Fluids and Mixtures*

E.W. Lemmon, M.L. Huber, M.O. McLinden, J.C. Rainwater, A.H. Harvey, D.G. Friend, and S.L. Outcalt

Objective: To develop reference thermodynamic surfaces for selected pure fluids and mixtures for calculating properties within the experimental uncertainties of measured data over large ranges of temperature, pressure, and composition.

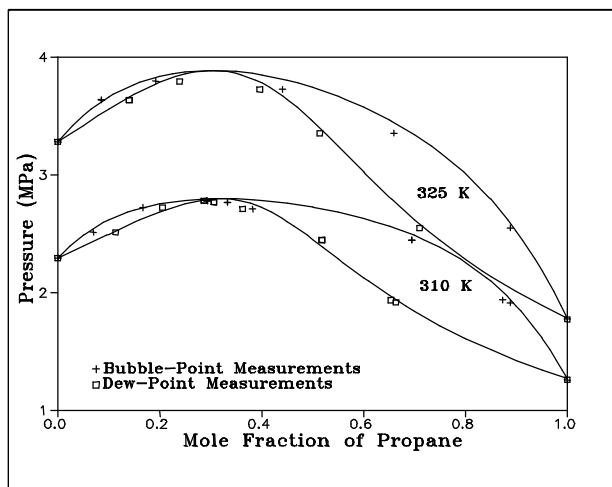
Problem: The thermodynamic properties of fluid systems are required in numerous industrial applications. In particular, accurate property information is needed for the working fluids used by such industries as power generation and refrigeration for design and operation of their technologies. Custody transfer considerations demand such data for commodity chemicals and energy-related fluids including natural gases. Finally, such reference quality information is needed in the development of more broadly applicable engineering formulations and in a variety of calibration applications. In these and other areas, NIST provides the infrastructure for the Nation's thermodynamic property needs.

Approach: The systems chosen for study are determined by our customer's stated and anticipated needs, and generally fall into such classes as refrigeration fluids, cryogenics, and natural gas systems, and are re-prioritized every few years based on industrial feedback. The general data infrastructure at NIST also demands that certain systems be described to fill important gaps and to serve as a basis for the predictive models used for less well-characterized systems. The models are usually in the form of Helmholtz energy equations, which allow calculation of all thermodynamic properties in the fluid phases in a consistent manner, and which are based on fundamental statistical mechanics, on empirical use of available data, and on advances in statistical correlation techniques. This work is coordinated with the experimental efforts of the Division.

Results and Future Plans: In conjunction with collaborators from Germany, a new thermodynamic formulation for nitrogen has been developed based

on a structural optimization algorithm, that provides a dramatic reduction in the uncertainties associated with the NIST cryogenic flow calibration facility. A reference equation was completed for the refrigerant R143a (CF_3CH_3). Several other important refrigerants, as well as systems such as toluene and alcohols, are under study. (Our general program on refrigerants and work on the ammonia-water binary system are described in Technical Highlights 13 and 14, respectively.)

A mixture model, based on a corresponding states algorithm for the excess Helmholtz energy and reference quality formulations for the constituents, has been developed. This model has undergone testing as part of our commitment to the International Energy Agency in its study of mixtures containing R32 (CH_2F_2), R125 (CF_3CHF_2), and R134a ($\text{CF}_3\text{CH}_2\text{F}$), and forms the core of the thermodynamic modeling capability in NIST Refprop. The accompanying figure shows the model's extension to the calculation of phase behavior for propane + R32 mixtures.



Publications:

Lemmon, E.W. and Jacobsen, R.T., "A Generalized Model for the Thermodynamic Properties of Mixtures," *Int. J. Thermophys.* (in press).

Outcalt, S.L. and McLinden, M.O., "An Equation of State for the Thermodynamic Properties of R143a (1,1,1-trifluoroethane)," *Int. J. Thermophys.* (in press).

4. *Transport Property Models for Fluids*

D.G. Friend, R.A. Perkins, M.L. Huber, M.O. McLinden, E.W. Lemmon, A. Laesecke, J.C. Rainwater, and S. Kiselev (Inst. Oil and Gas Res., Russia)

Objective: To establish models to evaluate the viscosity and thermal conductivity of a variety of important pure fluids and mixtures to within uncertainties required by the relevant user community.

Problem: The viscosity and thermal conductivity of fluids and fluid mixtures are required in many engineering applications including those related to the refrigeration, petroleum, and natural gas industries. In addition to direct applications, reference quality formulations are used in the calibration of commercial instruments used to measure these properties. In certain contexts, transport properties can be used to ascertain stream composition, extent of reactions, product quality, etc., and, in other cases, they may be primary process design parameters. The data and modeling infrastructure provided by NIST promotes design innovation and optimization for industrial and commercial applications.

Approach: The transport property models developed at NIST are most easily transferred to our customers through standard reference databases such as NIST Refprop (see Technical Highlight 13) and NIST SUPERTRAPP, but they are also disseminated through traditional publications and our activities in various standards organizations. The models begin with an understanding of basic kinetic theory applied at the molecular level, incorporate empiricism based on conventional statistical approaches when necessary, and may involve significant approximations to account for poorly characterized constituents, multiparticle correlations, mixing effects, internal degrees of freedom, etc. This activity is very closely tied to the experimental measurements of viscosity and thermal conductivity conducted in the Division.

Results and Future Plans: An extension of our transport property extended corresponding states (ECS) model has enabled us to undertake the

significant challenge of calculating the transport properties of petroleum fractions, which may contain literally hundreds of components and which are only characterized by a few key parameters which can be easily determined. This new model is described in a forthcoming publication, and will be incorporated in a version of a database to be available from NIST. In the course of this work, a new reference fluid formulation for the viscosity of propane was required and a preliminary version has been developed. Reference quality equations were also developed for the transport properties of R134a ($\text{CF}_3\text{CH}_2\text{F}$) (as the basis for refrigerant calculations), as well as the thermal conductivity of propane and toluene (a calibration fluid) and viscosity of n-pentane (a calibration fluid). Studies of additional key pure fluids are underway, including a major improvement to our calculations of the viscosity and thermal conductivity of pure water.

Work has been completed on an extension to the ECS model for viscosity that yields a significant improvement in our ability to calculate this property for the refrigerants. Similar work is underway for the thermal conductivity. This approach will also be applied to natural gas systems. Finally, we have developed a new approach to provide accurate values for the transport properties of air at extreme temperatures and pressures as part of a project associated with advanced wind tunnel designs.

Publications:

Baltatu, M.E., Chong, R.A., Huber, M.L., and Laesecke, A., “**Transport Properties of Petroleum Fractions**,” *Int. J. Thermophysics* (in press).

Klein, S.A., McLinden, M.O., and Laesecke, A., “**An Improved Extended Corresponding States Method for Estimation of Viscosity of Pure Refrigerants and Mixtures**,” *Int. J. Refrig.* 20, 108 (1997).

5. *Critical Evaluation of Chemical Kinetics Data - New Tools and Old Problems*

W. Tsang, R.F. Hampson, V.I. Babushok (Guest Researcher), W.G. Mallard, D.H. Frizzell, J.J. Reed, F. Westley (Contractor), Y.A. Mirokhin (Guest Researcher), J.T. Herron (Contractor), and C-Y Lin (Contractor)

Objectives: To collect and evaluate data on the rates of gas phase chemical reactions needed for modeling natural and industrial processes; to develop new calculational tools for evaluating data on pressure-dependent rate constants.

Problem: Understanding complex chemical processes – such as those that occur in the atmosphere, a furnace or a chemical vapor deposition reactor – often requires a detailed model of the chemical changes that are occurring. To create such a model, one requires a rate for each reaction in the system, usually as a function of temperature. While much of this information exists, it is often fragmentary and difficult to find. In addition, older analyses of experiments have often proven to be incomplete and the resulting rate constants reported incorrect. In addition to the collection and evaluation of temperature-dependent rate constants, efforts are also needed to understand the dependence on pressure.

Approach: There are several components of this work. First, the technical literature is routinely searched and all publications presenting data on the rates of chemical reactions are retrieved, and data relevant to on-going evaluation projects are abstracted for use by evaluators. Second, the data are compared to other similar systems, and when possible, models of complex systems are developed and compared to experimental results. The resulting kinetic parameters are examined to determine trends in reactivity and associated bond energies implied by the kinetic parameters. Comparisons of these results with theoretical calculations are made. The results of these studies are published in the literature and distributed as electronic data sets. One of the most important methods of making the data available is via the Chemical Kinetics Database for use on personal

computers. Version 6.0 of this database, released in 1995, contains data relating to 8800+ reactant pairs.

Results and Future Plans: Production of a Windows version of the basic chemical kinetics software and entry system is progressing, and a Windows version of the Chemical Kinetics Database will be available in early FY98. In addition, a new set of tools for the analysis of complex unimolecular and recombination reactions has been developed. The analysis of data on these reactions has always been dependent on model calculations, the most common being the so-called RRKM model. The development of a detailed master-equation-based analysis of the thermal activation process of these complex systems has led to a better understanding of many recombination reactions for which there are multiple pathways. These reactions are especially difficult to model in cases in which radical recombination produces species that have sufficient energy to go into various other reactive channels as well as to return to the original products. The detailed solutions to these problems based on master equations have begun to yield predictive tools for these complex reactions. A long-range goal is to provide simple tools to allow the non-expert to perform pressure dependent calculations easily, perhaps as part of a single, integrated package.

Publications:

Tsang, W., Bedanov, V., and Zachariah, M.R., “Unimolecular Decomposition of Large Organic Radicals with Low Reaction Thresholds: Decomposition and Reversible Isomerization of n-Pentyl Radicals,” in *Berichte der Busengesellschaft fur Physikalische Chemie* (in press).

Atkinson, R., Baulch, D.L. Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J., and Troe, J., “Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VI - IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry,” *J. Phys. Chem. Ref. Data* (in press).

6. *Ab Initio* Prediction of Ionization Energies

R.D. Johnson III

Objective: To predict the ionization energies for important chemical species using modern methods of computational chemistry and to evaluate the methods for accuracy.

Problem: Many chemical properties can be related to the ionization energy of a molecule or radical, e.g., the electronegativity that correlates with chemical reactivity. The ionization energy can be problematic to measure, but is straightforward to calculate by *ab initio* methods. This is especially true for radicals. However, routine use of *ab initio* methods requires testing and validation to establish the accuracy and precision of predicted ionization potentials computed with a given method or level of theory.

Approach: *Ab initio* methods of quantum chemistry are powerful enough to generate ionization energies to better than 0.1 eV. The ionization energy is obtained by taking the difference between the calculated absolute energies of neutral and cationic species. The vibrational frequencies must be known or computed in order to obtain the correct zero point vibrational energy. The accuracy can be assessed by calculating the ionization energy of species with experimentally well determined ionization energies. Ongoing research is 1) exploring the accuracy of different levels of theory, and 2) exploring reaction schemes involving species with known ionization energies to improve accuracy by using calculated ionization energy differences in order to minimize systematic errors. This *ab initio* work is in collaboration with experimental work to determine ionization energies and thermochemical properties.

Results and Future Plans: Studies are underway on a series of stable fluorocarbon species, fluorocarbon radicals and species of atmospheric interest. The stability of simple perfluorocarbon cations had been questioned in the past, but *ab initio* calculations found them to be stable species. For example, the perfluoroethane cation has a C-C bond strength on the order of 90 kJ/mol, and perfluoropropane cation has a C-C bond strength on the order of 70 kJ/mol. Combined with calculated

electron affinities the electronegativities have been calculated for a series of fluorocarbon radicals. This allows for the prediction of reactivities in organic reactions, where the fluorocarbon radicals are used as protecting groups. The ionization energy of HNO was calculated to compare with photoelectron experiments and establish a heat of formation for this molecule of atmospheric importance.

Publications:

Kuo, S., Zhang, Z., Ross, S.K., Klemm, R.B., Johnson, R.D., Monks, P.S., Thorn, R.P., and Stief, L.J., “Discharge Flow-Photoionization Mass Spectrometric Study of HNO: Photoionization Efficiency Spectrum and Ionization Energy and Proton Affinity of NO”, J. Phys. Chem. A101, 4035, 1997.

7. *Thermophysical Properties of Gases Used in Semiconductor Processing*

J.J. Hurly, K.A. Gillis, and M.R. Moldover

Objective: To provide industry with high-accuracy data for modeling CVD (chemical vapor deposition) processes and for calibration of MFCs (mass flow controllers) used in semiconductor processing.

Problem: Many process gases are toxic, and/or corrosive, and/or pyrophoric. For such gases, measurements of their thermophysical properties are sparse and rarely accurate. Accurate thermophysical property data are required to model the hydrodynamics of the gas streams, *i.e.* the velocity and temperature profiles in the vicinity of the hot susceptor, together with the concentration and temperature gradients that evolve within the streams used in CVD processes. MFCs are used to deliver process gases (*e.g.* Cl₂, HBr, BCl₃, WF₆) for CVD and for other processes (*e.g.* plasma etching) throughout the semiconductor industry. Calibrated MFCs are needed to scale processes up from prototype to pilot plant and to production. The operation of MFCs depends upon heat transfer through the process gas; however, MFCs are sold based on calibrations for benign "surrogate" gases (such as N₂, CF₄, SF₆, and C₂F₆). Rationalization of this practice requires data for the density, heat capacity, thermal conductivity, and viscosity of the process gases as functions of temperature and pressure.

Approach: The Fluid Science Group will use acoustic techniques to measure the thermophysical properties of three classes of gases: (1) binary mixtures of CVD carrier gases with process gases, (2) pure process gases, and (3) surrogate gases. The Group will develop a comprehensive, reliable database for these gases that provides the heat capacity, thermal conductivity, viscosity, and the pressure-density-temperature relation for the gases and also diffusion coefficients for mixtures of the gases. The diffusion coefficient will be obtained from models for the intermolecular potentials between the carrier and the process gases.

Results and Future Plans: We have assembled and tested a facility in which acoustic techniques can be

used safely for measuring the properties of these hard-to-handle gases. During the upcoming year, we shall measure speed of sound in the seven gases that were identified by the SEMATECH MFC Working Group as having the highest priority. They are the process gases Cl₂, HBr, BCl₃, WF₆, and the surrogate gases CF₄, SF₆, and C₂F₆. From the data, we shall obtain the ideal-gas heat capacity and the equations of state with uncertainties of approximately $\pm 0.1\%$. Initially, the data will range from 0 C to 200 C and from 25 kPa to 400 kPa or 80% of the vapor pressure. The data will be extended to higher temperatures (until chemical instability becomes a problem) and transport property data will follow.

8. *Thermodynamic Data for the Industrial Application of Chemical Compounds*

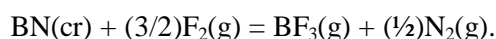
P.A.G. O'Hare and D.R. Kirklin

Objective: To obtain the basic thermodynamic data required for the industrial application of organic and inorganic materials.

Problem: Advances in the applications of many materials is limited by inaccurate or incomplete thermodynamic data. This can be particularly important in applications in which the phase of the material after processing determines key characteristics.

Approach: Fluorine and oxygen bomb calorimetric techniques are utilized to obtain the enthalpies of formation of the materials. This information is combined with data on the enthalpy increments to obtain a complete description of the thermodynamic properties of the material.

Results and Future Plans: During the past year, studies were completed on the fluorine-combustion calorimetry of several silicon compounds, including β - Si_3N_4 . Future studies will be concentrated on the (boron + nitrogen) system, in which four distinct solid modifications have been identified. Those are amorphous, wurtzitic (formed at high pressures), hexagonal, and cubic. The cubic form has a hardness surpassed only by diamond but is superior to diamond in its high-temperature stability. Accordingly, cubic boron nitride has high potential for use in cutting tools. Some of the techniques utilized in depositing boron nitride may yield other forms, in addition to the cubic. Thus, it is important to understand the conditions under which only cubic BN will be produced. Unfortunately, the (boron + nitrogen) phase diagram is not well defined. Preliminary studies have shown that hexagonal and cubic boron nitride react with fluorine in our bomb calorimeter in a simple and straightforward way:



Because the standard enthalpy of formation of BF_3 is already well established, measurements of the energies of reaction will give the standard molar enthalpies of formation and, thus, a relative ranking

of the stability of the different forms of BN. This information will provide a sound basis on which to construct a reliable phase diagram for the (boron + nitrogen) system to support technological applications.

Also during the past year, oxygen-combustion and differential-scanning calorimetric measurements were carried out on three structurally similar benzaldehydes: 1,4-benzenedicarboxaldehyde (terephthalaldehyde), 1,3-benzenedicarboxaldehyde (isophthalaldehyde), and 1,4-carboxybenzaldehyde. With the new data for the phthalaldehydes and the carboxybenzaldehydes, and data already available for the phthalic acids, estimations of the energetics of diacids, dialdehydes, and acid aldehydes are now possible.

Publications:

Kirklin, D.R. and Affefy, H.Y., "Enthalpy of Formation of 1,4-Benzenedicarboxaldehyde," J. Chem. Eng. Data (in press).

Tomaszkiewicz, I., Hope, G.A., Beck, C.M., III, and O'Hare, P.A.G., "Thermodynamic Properties of Silicides. VI. Pentamolybdenum Trisilicide (Mo_5Si_3). Fluorine Combustion Calorimetric Determination of the Standard Molar Enthalpy of Formation at the Temperature 298.15 K," J. Chem. Thermodynamics 29, 87 (1997).

O'Hare, P.A.G., Tomasziewicz, I., and Seifert, H.J., "The Standard Molar Enthalpy of Formation of β - Si_3N_4 by Combustion Calorimetry in Fluorine, and the Enthalpy of the α -to- β Transition at the Temperature 298.15 K," J. Materials Res. (in press).

9. *Measuring and Modeling Solute-Solvent Interactions in Supercritical and Subcritical Fluids*

T.J. Bruno and A.F. Lagalante

Objective: To develop and test predictive models for solubilities of compounds in alternative solvents at supercritical, near-critical, and subcritical conditions using a combination of both physical and chemical variables as input into an empirical multivariate statistical model.

Problem: As a result of the Montreal Protocol, many industrially important chlorinated solvents used in cleaning and extraction processes will become unavailable. The most important piece of thermophysical data to assess the feasibility of an extraction process is the solute-solvent phase equilibrium. Serious limitations exist in equation-of-state modeling approaches that use only physical properties of the solute and solvent to model supercritical and near-critical solute solubility.

Approach: Replacements for the chlorinated solvents are likely to come from fully or partially fluorinated alkanes, ethers, or ketones that possess negligible ozone depletion potential, as well as functionalized glycol ethers and siloxanes. Many of the fluorinated alternative solvents are gases under ambient conditions, and their thermophysical properties offer the promise of both conventional liquid extraction and the tunable solvent strength offered by near-critical and supercritical fluid extraction. In our approach, a given solution process is empirically modeled as the dependent variable in a multivariate statistical analysis. The independent variables to the multivariate statistical model include quantitative measurements of solute-solvent interactions and additional state-dependent terms. Solute-solvent interactions are quantified using the Kamlet-Taft solvatochromic chemical parameters. These parameters are empirically determined values of three solvent-solute interactions: acidity, basicity, and dipolarity-polarizability. Work is in progress to significantly extend the Kamlet-Taft parameters to the fluorinated solvents in the subcritical and supercritical phases as well as the glycol ethers and siloxanes at ambient conditions. The resulting models will aid in the

replacement of chlorinated solvents by making it possible to predict the solubility of industrially relevant compounds in alternative solvents.

Results and Future Plans: In recent years, we have designed and constructed numerous instruments for the quantitation of solubilities of solutes in subcritical and supercritical fluids. Solutes studied have ranged from classes of organometallic compounds (such as the metal β -diketonates) to physiologically active natural products (β -carotene, capsaicin). Recently, we have measured water-solvent partition coefficients for sets of organic solutes in fluorinated ethane solvents. The Kamlet-Taft parameters for the fluorinated ethane solvents have been measured using high-pressure equilibrium cells. Results show a constant basicity and density-dependent acidity and dipolarity-polarizability values over the gas-to-liquid density range. Kamlet-Taft parameters for the glycol ethers and siloxanes have been measured for both the pure compounds and aqueous solutions of the compounds. Based on the measured water-solvent partition coefficients and the measured Kamlet-Taft values for the fluorinated ethanes, a model was developed to predict the solute partition coefficients in 1,1,1-trifluoroethane and 1,1,1,2-tetrafluoroethane, as well as in carbon dioxide. In the future, we will model other types of equilibria, such as solubility and gas chromatographic retention times, in the alternative solvents. A predictive solubility model will suggest suitable alternative solvents and extraction conditions to substitute for an obsolete chlorinated solvent. Although initially the model will be tested using the pure fluorinated alternative solvents, we envision that the model can be applied to other classes of solvents as well as azeotropic mixtures of solvents.

Publication:

Lagalante, A.F. and Bruno, T.J., "Modeling of Water-Carbon Dioxide Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship," *J. Phys. Chem. A* (in press).

10. Measurements and Database for Adsorptive Separations

T.J. Bruno, J.E. Mayrath, H.J.M. Hanley, F. Tsvetkov (Daren Laboratories, Inc., Israel), and A. Lewandowska (Univ. Colorado)

Objective: To provide basic data to facilitate the design of efficient and effective adsorptive separations for process and environmental applications.

Problem: Adsorptive separation techniques represent a versatile and selective family of methods that is especially applicable to dilute solutions. This is a concentration regime that is particularly problematical and costly for many industries, including chemical processing, energy, pharmaceuticals, and almost all phases of environmental remediation. As currently practiced, the design of adsorptive separations relies greatly on intuition. Adsorbents are customarily characterized in terms of surface area and pore size distributions, which are concepts that do not adequately account for the actual structures and attractive potentials that increase the concentrations of adsorbates on the surfaces of adsorbents. Moreover, thermodynamic properties (such as isotherms and enthalpies) measured on "standard adsorbents" cannot fully account for porosity and adsorptive capacities for other adsorbates, nor can such measurements account for properties at conditions differing from those of the standard measurements. This situation makes the rational design of adsorptive separations extremely complex.

Approach: This project consists of a data-oriented effort and an experimental measurement and modeling effort. The data work encompasses a literature review and critical evaluation of the literature focused on theory and measurements concerning adsorption from the gas phase on carbon, zeolites, and novel materials (polymers, urea, clathrates, etc.). Other physical property measurements of the adsorbents are correlated (where possible) with the customary or classical adsorption isotherms and areas and porosities. The current experimental effort concerns the enthalpy of adsorption of pollutants on unmodified clays (and clays modified with surfactants), and also the measurement of the skeletal density of adsorbents.

We are using a chromatographic approach to measure the enthalpies, in which the clays (laponite, bentonite, montmorillonite, etc.) are deposited on glass spheres, which are then packed into columns. The temperature dependence of the specific retention volume provides the enthalpic information. The skeletal density apparatus consists of a microbalance enclosed in a vacuum chamber. Necessary gas manifolds allow the introduction of helium and other gases at known temperatures and pressures, and therefore, densities. One then measures the mass at several gas densities at several sample temperatures, ultimately yielding the adsorbent skeletal density.

Results and Future Plans: The results of the comprehensive literature search have been compiled into a 2000 entry database that is searchable by a variety of keyword approaches. Data are being added on an ongoing basis, after a critical evaluation is done. The results of the literature review have revealed that there are no recognized or *de facto* standard adsorbents suitable for characterization. Surface area and pore size distributions were found to be virtually meaningless for materials that were thought to provide material separation on the basis of size and/or shape. The skeletal density apparatus is fully operational and is now undergoing performance testing with a variety of carbonaceous materials and well-characterized synthetic adsorbents. Enthalpy of adsorption measurements have been completed for a large number of hydrocarbons and pollutant species on laponite clay, and on a laponite clay that had been modified by an organic surfactant. These data provide an insight into the relative strength of the adhesion of such pollutants on these common adsorbents. Correlations have emerged that relate structural features such as carbon number to the measured enthalpy. The measurements on the organic-modified laponite provide insight into the mechanism of pollutant adsorption and partitioning in real soil systems. In the next year, enthalpy of adsorption work on more highly branched hydrocarbons will be performed on both the modified and unmodified clay surfaces.

11. Measurements and Data for Membrane Separations

J. Pellegrino, M.R. Yetzbacher, J. Portnoy, T. Nguyen, B.R. Mattes (Los Alamos National Laboratory), and **M. Guiver** (National Research Council of Canada)**Objective:** To develop improved quantitative structure/property prediction methods for polymeric membrane materials based on high quality measurements of sorption and transport of gases and vapors in several well-characterized systems and to compile property data on industrially-significant materials used for membrane-based separations.

Problem: Although polymeric materials are used in membrane and adsorptive separation processes, a significant barrier to the development of new materials and optimum use of existing materials is the lack of *a priori* predictive capabilities for the transport properties of mixtures in any selected polymer.

Approach: This program has a measurement and modeling component and a data component. Measurements of gas (and vapor) sorption and diffusion in polymers are critical for development of techniques to predict transport properties. These measurements provide a means to compile the effects of both chemical and structural subgroups in the polymer, and ultimately, to delineate rational design criteria for separations. Through our collaborations with Los Alamos National Laboratory and the National Research Council of Canada, we have access to materials whose chemistries can be varied in well-defined ways. In addition, the polymers under study (polysulfone, polyperfluorosulfonic acid, polytrimethylsilylpropyne, and polyaniline) represent both commercial and cutting-edge materials. Improved processes for obtaining high purity oxygen and nitrogen from air, processing natural gas, recovering hydrogen from refinery streams, recovering and purifying olefin streams, and purifying water are examples of important industrial uses of membranes. The data component of this research program consists of the development of an Internet accessible database of polymeric material properties that are important for membrane separation design.

Results and Future Plans: Four (two fully automated) sorption apparatus (based on pressure decay methods) are currently in operation. During the past year, data have been obtained for determining the film density and sorption and diffusion coefficient for various permanent gases in the temperature range 293-308 K in polyaniline film doped with HF, and in the unmodified and silane-derivatized polysulfone base polymer. Also, refurbishment and recalibration of the multicomponent gas flow apparatus for measuring transport of gas and vapor mixtures through membranes were completed in preparation for designating it as a user test facility. An initial version of the membrane technology database, containing gas transport properties in hundreds of polymers, has been completed and is accessible internally via World-Wide-Web browser programs. A variety of software tools is still being developed to provide more complete querying capabilities and report generation. This work addresses a need within the chemical engineering community for comprehensive, critically evaluated information on separation membranes, and how these membranes interact with important chemical feedstock components. The current version of the database includes permeability, solubility, and diffusion coefficients; ideal and mixed gas separation factors; temperatures; primary reference; monomer repeat unit structure; and common names and abbreviations. Future work will expand the number of polymers and include additional solute interaction parameters of feed materials with the membrane materials. Membrane properties to be added include transition temperatures of membrane polymers, densities, and elastic moduli.

12. Experimentally Validated Database for Neutral/Ion Kinetics for Plasma Processes

L.W. Sieck, J.T. Herron (Contractor), D.S. Green (U. Md), T.J. Buckley, and E. P. Hunter

Objective: To develop a laboratory-validated database for modeling the processes associated with non-thermal plasma treatment of gas streams.

Problem: Substantial advances in effective manufacturing and environmental cleanup can be achieved by exploiting non-thermal plasma treatment. In such discharges, chemical change is driven by a variety of processes including ionization, molecular excitation, ion-electron recombination, fragmentation of ions and excited molecules, and reactions of radicals, atoms, and ions. The quantitative modeling of these processes requires a reliable database describing the key elementary kinetics involved.

Approach: The program has centered around the creation and validation of an ion chemistry database for use in modeling plasma processes. In addition, a neutral-chemistry component will also be pursued to describe more completely the total chemistry. Creation of the database involves data collection and evaluation, experimental measurements of specific rate parameters, and verification of the model with the new NIST hybrid high-pressure mass spectrometer system, scheduled for full operation by January 1998.

Results and Future Plans: Current efforts are focused on the primary kinetics operative in plasma removal of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) from humid air streams typical of jet-engine test beds and from diesel sources. The first effort was a survey and assessment of the available literature pertinent to positive ion chemistry in both wet and dry air at one atmosphere, and a recommended database was created for the temperature range 300-700 K. The database includes pressure effects and the conversion from third- to second-order kinetics (which is of particular importance in modeling atmospheric reactions), as well as switching reactions and the formation of cluster ions, and the effect of applied electric fields on the various rate

parameters. The goal of this activity is to develop a reliable predictive scheme for air-only atmospheric-pressure reactors. This predictive scheme is based on modeling of the low-pressure scheme, which was validated and modified by comparison with direct results from the NIST high-pressure mass spectrometer.

During the past year, additional lab diagnostics were also carried out with toluene (as a representative VOC), and these studies will be extended in detail next year to CCl_4 , which is one of the four target molecules chosen for intensive study by the IUPAC Hazardous Waste Task Force. These measurements demonstrated the dramatic effect that these additives have on the air system, including an apparently complete quenching of the NO_x ion chemistry. In the coming year, we will create a compact chemical kinetics database for ion chemistry at one atmosphere incorporating key reactions representative of VOCs that influence the destruction of NO_x during non-thermal plasma treatment. A generic recommended database for negative ion kinetics in humid air at atmospheric pressure including trace components such as O_3 , NO , NO_2 , and CO_2 will also be assembled. Laboratory validation of the competitive ion kinetics and important parent-daughter relationships will be conducted as required. The neutral database will also be extended to include excited state reactions of N_2 , O_2 , N , and O with both NO_x and $\text{C}_1\text{-C}_2$ hydrocarbons.

Publications:

Herron, J.T. and Green, D.S., "Evaluated Chemical Kinetics Data for Neutral Reactions in Humid Air Plasmas."

Sieck, L.W., Herron, J.T., and Green, D.S., "Evaluated Chemical Kinetics Data for Positive Ion Reactions in Humid Air Plasmas. "

13. Thermophysical Properties of Alternative Refrigerants

M.O. McLinden, D.R. Defibaugh, K.A. Gillis, C.D. Holcomb, M.L. Huber, J.J. Hurly, A.R. Laesecke, E.W. Lemmon, J.W. Magee, M.R. Moldover, S.L. Outcalt, R.A. Perkins, and L.A. Weber (Contractor)

Objective: To provide industry with high-accuracy property data and models for alternative refrigerants and refrigerant mixtures.

Problem: The chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants must be replaced with fluids, which do not deplete stratospheric ozone. To evaluate the energy efficiency, capacity, etc. of any fluid in a thermodynamic cycle, or to design equipment using a new fluid, knowledge of the thermophysical properties is required.

Approach: Our work on alternative refrigerants represents a comprehensive approach to a major problem and has been supported by multiple government agencies and industry groups. Our work in this area includes experimental measurements and the compilation and evaluation of literature data. These data provide the input information for developing the models that form the basis of the REFPROP database. Also included are technology transfer activities and participation in international collaborations.

Results and Future Plans: The work on alternative refrigerants is shifting increasingly to mixtures and to transport properties. We have completed viscosity measurements on mixtures of R32 (CH_2F_2), R125 (CF_3CHF_2), R134a ($\text{CF}_3\text{CH}_2\text{F}$), and propane. Complementary work on the thermal conductivity is in progress. We have measured the viscosity of several fluorinated ethanes and propanes. Interest is increasing in the "natural refrigerants," and we have completed comprehensive measurements of the heat capacity and of the PVT and VLE behavior of the propane/isobutane system. Similar comprehensive measurements have been completed on several mixtures of the HFCs. We have also performed more limited thermodynamic measurements on several "developmental" fluids, such as the fluorinated butane, HFC-338mccq

($\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{F}$). These data form the basis for evaluating and improving the mixture Helmholtz model for the thermodynamic properties (Technical Highlight 3) and an extension of the ECS model for transport properties (Technical Highlight 4).

A complete revision of the Refprop database is in the review process and will be released early in 1998. In the past year, we have added new fluids, such as HFC-245fa ($\text{CF}_3\text{CH}_2\text{CHF}_2$), and incorporated new or improved models for the transport properties (Technical Highlight 4) and surface tension. We have also collected literature data on more than 75 refrigerant mixtures and used them to fit the parameters in the mixture Helmholtz energy model (Technical Highlight 3). In the international arena, NIST coordinated a comparison of refrigerant mixture models through Annex 18 of the International Energy Agency. This comparison showed the mixture Helmholtz energy model developed at the University of Idaho and NIST to have the best combination of accuracy and generality among the five models considered. We are in the process of developing a comprehensive formulation for the thermal conductivity of R134a under the auspices of the IUPAC Subcommittee on Thermophysical Properties. We also coordinated the revision of tables of refrigerant properties appearing in the 1997 ASHRAE Handbook of Fundamentals.

Publications:

Defibaugh, D.R., Carrillo-Nava, E., Hurly, J.J., Moldover, M.R., Schmidt, J.W., and Weber, L.A., "Thermodynamic Properties of HFC-338mccq, $\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{F}$, 1,1,1,2,2,3,3,4-Octafluorobutane," J. Chem. Eng. Data 42, 488-496 (1997).

Lemmon, E.W., "Evaluation of Thermodynamic Property Models for Mixtures of R-32, R-125, and R-134a," IEA Heat Pump Centre, Sittard, The Netherlands (in press).

14. Ammonia-Water Mixtures for Use in Power Cycles

D.G. Friend, J.C. Rainwater, A. Nowarski (Univ. Cracow, Poland), R. Tillner-Roth (Univ. Hannover, Germany), C.D. Holcomb, J.W. Magee, R.A. Perkins, W.M. Haynes, T. Lüddecke (Univ. Hannover, Germany), S. Kiselev (Inst. Oil and Gas Res., Russia), E.B. Thorin (Royal Inst. Tech., Sweden)

Objective: To establish standard reference thermophysical property surfaces for mixtures of ammonia and water over a broad range of temperature, pressure, and composition.

Problem: Drastically redesigned power plants have been proposed which use the binary ammonia-water system as a working fluid, and dramatic increases in efficiency have been predicted. Several companies have obtained license agreements to implement this approach. Critical design decisions and corporate risk analysis require property parameters that are not currently available. In addition to these engineering and other practical concerns, problems in the optimization of these new cycles and in the development of performance warranty protocols have not been resolved because of uncertainties in the thermophysical properties of the working fluid. This binary system is also the working fluid in some refrigeration applications, including prospective domestic heat pump and air conditioning technologies; the optimization of designs for these systems also requires reliable standard property information.

Approach: The project has required an extensive bibliographic study and evaluation of existing data; details concerning the required data and tolerances for industrial application are also needed. Experimental measurements will be obtained for selected properties at the most important state points; these include measurements of the VLE surface, density, isochoric heat capacity, thermal conductivity, and viscosity. Some apparatus modifications and development are required to perform the measurements. The modeling effort includes studies based on scaling theory to describe the high pressure region of the phase boundaries, as well as several versions of an extended corresponding states (ECS) algorithm. These must

be modified to account for the behavior of this system. Additionally, a two-fluid Helmholtz energy model is being developed to describe the thermodynamic surface of the mixture.

Results and Future Plans: A report of a workshop on the thermophysical properties of ammonia-water mixtures, held by NIST and geared to industrial users of this information, was published this year. Efforts continued in the areas of data collection and evaluation, and a two-fluid Helmholtz energy model has been optimized to the available data. The ECS model now incorporates state-dependent shape factors and seems to show promise in allowing extrapolation into the high temperature regions of major interest. A set of measurements of the isochoric heat capacity has been completed, with temperatures to 523 K, for ammonia-rich mixtures. (See Technical Highlight 16 for a description of this experiment and apparatus.) Preliminary comparisons with the models indicate that further refinement of the models may be required. Work will continue on viscosity and thermal conductivity.

Publications:

Friend, D.G. and Haynes, W.M., "**Report on the Workshop on Thermophysical Properties of Ammonia/Water Mixtures,**" NISTIR 5059 (1997).

Nowarski, A. and Friend, D.G., "**Application of the Extended Corresponding States Method to the Calculation of the Ammonia-Water Mixture Thermodynamic Surface,**" Int. J. Thermophys. (in press).

Van Poolen, L.J. and Rainwater, J.C., "**Critical-Region Model for Bubble Curves of Ammonia-Water with Extrapolation to Low Pressures,**" Fluid Phase Equilibria (in press).

15. *Database for the Chromatographic Analysis of Natural Gas*

T.J. Bruno

Objective: To provide an efficient, fast, and reliable method for identifying in both the laboratory and the field the heavier components of natural gas (the C₆+ fraction, that is, species that have a carbon number in excess of 6), and natural gas treatment materials.

Problem: The design of many processes involving natural gas, as well as the custody transfer of natural gas, rely on an accurate chemical analysis of the gas composition. However, the most common analysis of natural gas at present considers only the lightest components, and inclusion of the heavier fraction into the analysis (an approach called the "extended natural gas analysis") is a complex problem. In particular, natural gas consists of upwards of 400 organic and inorganic constituents, most of which occur naturally, and some of which are introduced intentionally during processing. Moreover, the composition varies with season, with source-well history, and with short-term usage and storage history. Thus, a fast, low-cost, and reliable method is required for the efficient commerce and use of this vital natural resource.

Approach: Gas chromatography offers an economical and accurate solution to the problem of the extended natural gas analysis. In addition to being one of the most well understood and economical analytical methods available, it is very amenable to field applications. What is needed is an interactive database that can be incorporated into the control and analysis software of both laboratory and field gas chromatographic instrumentation. We have approached the problem of standardizing and automating the extended natural gas analysis through the measurement of standard chromatographic retention parameters on the most useful stationary phases available, and also on some novel developmental phases. The standard retention parameters that we have measured include net retention volumes, relative retentions, and Kovats retention indices. These parameters are corrected for instrumental variation and are, therefore, reproducible from instrument to instrument. The measurements are performed on a specially modified

commercial gas chromatograph that provides highly accurate retention information. The column temperature dependence of each retention parameter is modeled with appropriate equations to allow predictions at all relevant temperatures. These models then form the heart of an interactive database that allows offline identification of peaks, and also the optimization of more complex analyses.

Results and Future Plans: The measurement of all standard retention parameters at four or more column temperatures has been completed for a series of representative C₆+ hydrocarbons on eight stationary phases. In addition, similar measurements have been completed for odorant compounds on four stationary phases. These stationary phases include the well-known methyl silicones and their more useful derivatives, porous polymer and solid adsorbent SCOT (surface coated open tubular) columns, and also some novel stationary phases that include sol/gel phases and clay phases. During the next year, we will add measurements on additional methyl silicone derivatives, and at least one modified adsorbent CLOT (coated layer open tubular) column. All of the modeled data will be entered into the database, an initial version of which has been released for testing and evaluation.

Publication:

Bruno, T.J. and Wertz, K.H., "Gas Chromatographic Retention Parameters: The Basis of Chromatographic Peak Identification for Extended Natural Gas Analysis," Proc. Institute of Gas Technology Symposium on Natural Gas Quality, Orlando, FL (1997).

16. *Adiabatic Twin-Cell Calorimeter for Isochoric Heat Capacity Measurements*

J.W. Magee, R.A. Perkins, D.G. Friend, and M.O. McLinden

Objective: To establish a calorimetric apparatus to accurately measure the isochoric heat capacity of corrosive or reactive substances over wide ranges of temperature and pressure.

Problem: Calorimetric data spanning wide ranges of temperature and pressure are needed to validate predictive models for thermodynamic properties of working fluids, especially those under consideration for advanced power cycles, refrigeration cycles, and a wide variety of industrial processes. Accurate isochoric heat capacities are especially useful because they provide a sensitive test of such models.

Approach: An extensive array of techniques has been developed to measure heat capacity. Of these techniques, the adiabatic method is generally accepted to give the most accurate results. Our research group has employed the adiabatic method for heat capacity measurements for more than 35 years. Goodwin developed a low-temperature adiabatic calorimeter, which was later modified for automated measurement and control. It has been used to measure constant-volume heat capacities (uncertainty of 0.5 to 2%) for many fluids at temperatures from 20 to 345 K, and at pressures to 35 MPa. In the planning stages of this work, we recognized a need to augment our existing measurement capabilities by developing a new calorimeter that would extend the upper temperature limit to 700 K, without a compromise in accuracy.

In the adiabatic method, heat exchange between the calorimeter and its environment is eliminated as long as a temperature gradient does not exist. However, in actual practice, the maintenance of a zero temperature gradient is an ideal situation that cannot be realized. Thus, even the most carefully conducted calorimetric experiment results in some heat loss, requiring a correction to the data. Nevertheless, this correction can be minimized by automatic adjustment of the temperature of the surrounding jacket to follow that of the calorimeter. We may realize a further refinement by employing a

twin calorimeter design, thus eliminating such a correction. Twin devices employ two calorimeters that are as nearly identical in construction as possible, supported in nearly identical surroundings, resulting in the same heat losses. In the present work, we combine the features of twin calorimeters with the adiabatic method, with the goal of virtually complete elimination of the heat-loss correction.

Results and Future Plans: A high-temperature adiabatic calorimeter has been developed to measure the constant-volume specific heat capacities of both gases and liquids, especially fluids of interest to emerging energy technologies. The chief design feature is its nearly identical twin-cell arrangement, which allows accurate measurement of energy differences without large corrections for energy losses due to thermal radiation fluxes. The cells were constructed from Inconel-718, a high-strength steel with excellent corrosion resistance. Operating conditions for the calorimeter cover a range of temperatures from 250 to 700 K at pressures up to 20 MPa. Performance tests were made with a sample of twice-distilled water. Heat capacities for water were measured from 300 to 420 K at pressures to 20 MPa, a range where accurate heat capacity data already exist and have been incorporated into an internationally accepted formulation. The measured heat capacities differed from those calculated with this formulation with a root-mean-square fractional deviation of 0.48%. Measurements of the heat capacities of industrially important ammonia/water mixtures have been completed.

Publication:

Magee, J.W., Blanco, J.C., and Deal, R.J., "A High-Temperature Adiabatic Calorimeter for Constant-Volume Heat Capacity Measurements of Compressed Gases and Liquids," J. Res. NIST (in press).

17. *Thermodynamic Data for Environmental Fate and Risk Analysis*

D.G. Archer, M.W. Chase, D.R. Kirklin, R.D. Levin, and P. A. G. O'Hare

Objective: To provide thermodynamic information necessary for prediction of movement of heavy metals through ground waters (aquifers) and surface waters, and for prediction of remediation yields in treatment methodologies.

Problem: The environmental fate of a heavy-metal contaminant in an aqueous environment is determined by the extent of many competing reactions. The competing reactions include precipitation reactions, reduction-oxidation reactions, and ion-exchange reactions with the geological materials present. The extent of reaction for these types of processes is determined by the thermodynamic properties for the reaction in the aqueous system. This is particularly true for movement of contaminants in aqueous environments because known diffusion laws predict mass flux to be dependent on concentration gradients. Prediction of the level of contamination of aquifers and surface waters, as well as the prediction of the rate of migration of contaminants through these waters, is accomplished through calculational models (simulators). Therefore, the validity of any particular simulator's calculated distribution of a noxious contaminant is heavily dependent on the validity of the thermodynamic information for the competing reactions that is incorporated into the simulator. However, much of the thermodynamic information required to execute these calculations is not of sufficient accuracy to make the calculations meaningful. This is true not only for many heavy-metal containing species but also for some common ions with which heavy metals come into contact in a typical aqueous environment.

Approach: We intend to generate accurate thermodynamic properties of heavy-metal containing species and the common ions with which these species come into contact. Examination of the status of the literature regarding these properties will be conducted. These examinations will identify the relevant measurements described in the literature as well as document previous NIST tabulations of thermodynamic properties for these chemical species.

From these analyses, the measurements necessary to determine accurately the thermodynamic properties will be identified and conducted. A data-handling structure will be constructed that allows simultaneous evaluation of thermodynamically consistent properties for the desired species.

Results and Future Plans: This year, an analysis of previously reported thermodynamic properties for selected cadmium-containing compounds was prepared, as was an analysis of the thermodynamic properties of the potassium chloride + water system. (Potassium chloride is also a standard used in isopiestic measurements and for calibrating calorimeters.) An enthalpy of solution calorimetry laboratory was established this year; enthalpy of solution measurements contribute to the knowledge of how solubilities and other reactions change with respect to temperature. During the next year, analyses of the literature on the thermodynamic properties of common species containing mercury, chromium, lead, zinc, and manganese, similar to that for cadmium, will be completed. Measurements for selected species will be initiated, mass-flow calorimetry capabilities will be added, and construction of the data-handling system will be started. Also expected is initiation of a program to determine accurate thermodynamic properties of "key" substances. The "key" substances are required to extract the properties of a heavy-metal containing reactant from the measured properties of a reaction.

Publication:

Archer, D.G., "Enthalpy Increment Measurements for NaCl(cr) and KBr(cr) from 4.5 to 350 K. Thermodynamic Properties of the NaCl + H₂O System. 3," J. Chem. Eng. Data 42, 281-292 (1997).

18. Cavity Ring-Down Technology for Kinetic and Mechanistic Studies

J.W. Hudgens, R.E. Huie, and A.C.R. Pipino

Objectives: To improve the accuracy, precision, and sensitivity of optical absorption measurement protocols and to use these to measure chemical reaction rates in gas and liquid phases and at interfaces.

Problem: The development of accurate computer models of incineration, semiconductor processing, atmospheric chemistry, and solution chemistry requires accurate reaction rate coefficients for the key chemical reactions. In turn, such reaction rate measurements require accurate determinations of low concentrations of reactants and products as functions of time. For most species, optical absorption can measure concentrations very selectively, but the sensitivity is often insufficient to allow rate measurements.

Approach: We are developing cavity ring-down (CRD) optical absorbance measurement technology to meet the requirements imposed by chemical kinetics experiments in gas and condensed phases.

Results: This year, we used CRD detection to measure reactions of the propargyl radical in a slow-flow flash photolysis reactor. Our CRD studies determined the absolute absorption cross-section of propargyl radicals at 332.5 nm. Additional experiments measured the self-reaction rate coefficient for the propargyl radical and the rate coefficient for the propargyl + oxygen association reaction. Reactions involving propargyl radicals are believed to govern the production of soot in hydrocarbon flames. We also demonstrated the first application of CRD technology to measurements of condensed matter by constructing a right-angle cavity containing a fused silica Pellin-Broca prism. In this configuration, evanescent waves emanating from the internally reflecting surface of the Pellin-Broca probed the species residing on its surface. When we exposed this surface to gas-phase I_2 , the CRDS signal showed that the evanescent wave was increasingly attenuated as the surface became saturated with adsorbed I_2 . We found that the detection sensitivity for surface adsorbed iodine was less than 0.04 monolayer.

Future Plans: During the next year, we will use CRD spectroscopy to determine rates of gas-phase reactions that involve halogen monoxide, ethyl, methyl, peroxy, and propargyl radicals. We anticipate that the improved sensitivity obtained with CRD detection will also enable us to obtain accurate rates for bimolecular reactions between two *different* free radicals; if successful, such experiments should allow explorations of sparsely studied but important topics in chemical kinetics. We will also use our novel optical devices to study chemical reaction rates in the liquid phase.

Publications:

Atkinson, D. B. and Hudgens, J. W., "Propargyl Radical Kinetics Measured Using Ultraviolet Cavity Ring-Down Absorption Spectroscopic Detection: Self-reaction and Oxygen Addition," J. Phys. Chem. A (in press).

Atkinson, D.B. and Hudgens, J.W., "Chemical Kinetic Studies Using Ultraviolet Cavity Ring-Down Spectroscopic Detection: Self-reaction of Ethyl and Ethylperoxy Radicals and the Reaction, $O_2 + C_2H_5 \rightarrow C_2H_5O_2$," J. Phys. Chem. A **101**, 3901 (1997).

Pipino, A.C.R., Hudgens, J.W., and Huie, R.E., "Evanescent Wave Cavity Ring-Down Spectroscopy with a Total-Internal-Reflection Minicavity," Rev. Sci. Instrum. **68**, 2978 (1997).

Pipino, A.C.R., Hudgens, J.W., and Huie, R.E. "Evanescent Wave Cavity Ring-down Spectroscopy for Probing Surface Processes," Chem. Phys. Lett. (in press).

19. *The NIST Mass Spectral Database - Fully Evaluated*

S.E. Stein, A. Mikaya (Contractor), Zhu Damo (Guest Researcher), D. Tchekhovskoi (Contractor), C.L. Clifton, and W.G. Mallard

Objective: To provide the mass spectral community with a fully evaluated mass spectral database and with tested and documented search algorithms that will enable the positive identification of unknown organic compounds using gas chromatography/mass spectrometry (GC/MS).

Problem: Modern organic analytical chemistry is critically dependent on instrumental analysis. For qualitative analysis, there is no better tool than the mass spectrometer. Like many other analytical techniques, it is best used with a library of reference spectra. Even with good reference spectra, the data must be processed correctly. Robust algorithms that have been thoroughly tested to eliminate flaws are needed.

Approach: The next release of the NIST Mass Spectral Database will be fully evaluated. In particular, every one of the more than 130,000 spectra will have been assessed by at least one expert, and all questionable data by two experts. In addition, a number of advances in the algorithms for searching the database have been developed and extensively tested, both for their inherent functionality and to compare them to other search algorithms. The best algorithms are incorporated into the NIST search software.

Results and Future Plans: During FY97, a detailed examination of the data for all compounds in the database was completed. This effort is the first time such a large collection of scientific data from so diverse a set of experimenters has ever been evaluated. The data were examined for reasonable neutral losses, for air peaks, for impurities (either solvent or other related compounds), and for errors in transcription of the data from the original source. In every case where a change had to be made, agreement between at least two evaluators was required. The analysis was always conservative; if a given spectrum or spectral feature was not clearly in error, it was not changed. On the other hand, when the data were so suspect that they were impossible to

repair, they were removed from the database. In some cases where there was no alternative spectrum, this meant that the compound itself was removed from the database. Again, the decision was made to emphasize the quality of the final database and not the sheer size of the database. The resulting database represents the very best collection of mass spectral data ever assembled.

To make the database more useful to the GC/MS community, work has started on the addition of retention indices to the database. The retention index is a measure of the time it takes a compound to elute from the GC column. For many compounds that might otherwise be confused using mass spectra alone, the retention index makes it possible to make a more definitive identification. An example of an important class of compounds for which retention time data are especially useful is the hydrocarbons, many of which have very similar mass spectra. The first stages of compiling and entering retention index data have begun. Tools are being developed to evaluate the data and to use the data to predict retention parameters for compounds for which experimental data are not available.

20. *Automated Gas Chromatography/ Mass Spectral Decomposition and Analysis - Tools for Automating and Improving the Use of GC/MS Instruments*

S.E. Stein, O. Toropov (Contractor), A. Rumiantsev (Contractor), W.G. Mallard, and J.J. Reed

Objective: To develop and test algorithms for automatically deconvoluting and analyzing GC/MS data files using a target library of compounds.

Problem: The program currently underway has been fully funded by the Defense Special Weapons Agency (DSWA) to provide a method for analyzing for chemical weapons banned under the Chemical Weapons Convention. The software implementing the algorithms must provide full blinding of the analysis process so as not to compromise the proprietary data of treaty participants. In general, the analysis of GC/MS data files for complex mixtures can be time consuming and error prone. The normal method of doing a background subtraction to extract the single component can be essentially impossible in a complex mixture because there is no background. Even in only moderately complex chromatograms, a manual subtraction can produce seriously erroneous results.

Approach: A detailed noise analysis is performed, followed by a deconvolution of each of the peaks in the total ion chromatogram based on the individual ion chromatograms. The resulting eluents are then compared to reference spectra using a series of algorithms that take into account the degree of confidence that an analyst would have in the deconvoluted peak. The identification is presented with a confidence measure. The process of extracting the distinct eluents (or components) out of a complex data file breaks down into four parts: noise perception and evaluation, component perception, signal extraction, and compound identification. The noise perception and evaluation is central to the analysis since the recognition of the difference between a "real" peak caused by a compound eluting from the column and a "false" peak caused by noise depends upon a knowledge of the nature and size of the noise. Once the noise is

understood, the individual components can be extracted. The extraction of the signal involves examining the overlap of components and removing mass spectral peaks associated with a different eluent.

Results and Future Plans: The algorithm has been tested extensively using as a target library of chemical weapons agents. Over 30,000 data files have been examined to ensure that the algorithm does not produce false positives. At the same time, a number of experiments have been performed with low concentrations of target compounds similar to chemical agents to demonstrate that the algorithm is sensitive enough to detect all true positives at analytically useful concentrations. The results of these tests have shown that the algorithms used in the development of the software are robust and capable of automated and blinded analysis. Work is continuing on refining the algorithms to reduce the incidence of false identifications by making use of data other than the mass spectra. The use of retention indices is central to the further reduction of false positives. The software developed here has been adapted by the Organization for the Prohibition of Chemical Weapons (OPCW) for use in all inspections involving GC/MS instrumentation.

21. *Rheometry and Structure of Complex Molecular and Macromolecular Systems*

H.J.M. Hanley, B.D. Butler, C.D. Muzny, G.C. Straty, M.Y. Lin (*Exxon Research and Engineering*), and **T.M. Slawewski and C.J. Glinka** (*NIST Center for Neutron Research*)

Objective: To investigate the relationship between the structure and viscometric functions of complex molecules, macromolecular systems, colloids, and gels and to develop a metrology that combines radiation scattering with rheometry.

Problem: The flow properties of a complex system can be predicted or manipulated if the relationship between its structure (particle positional order and/or orientation) and rheological characteristics is understood. The structure can be determined by radiation scattering and can be coordinated with data measured independently from a rheometer or viscometer. The behavior, however, of macromolecular, and especially polymeric, solutions can be very sensitive to preparation history. Hence, the scattered intensities and the rheometric functions should be measured simultaneously. Our project is the first to measure scattered neutron or light intensities simultaneously with data from a modified rheometer.

Approach: We investigate the structure of a complex system using the small angle neutron scattering (SANS) spectrometers at the NIST Center for Neutron Research (NCNR), Gaithersburg, and our light scattering facilities in Boulder. The system can be studied at rest or when subjected to a shear or stress. The scattering cell is an adapted Couette cell controlled by a constant stress rheometer that is placed in the neutron or light beam. In this way, simultaneous radiation and viscometric data can be obtained. The apparatus is capable of high accuracy measurements for viscosities that can range over ten orders of magnitude, and the combination of neutron and light radiation allows us to investigate length scales of the macromolecular system of interest ranging from about 5 nm to 10 : m.

Results and Future Plans: The scattering/rheometric apparatus has recently been constructed. We have made simultaneous

measurements of the viscosity and the anisotropic scattering patterns as a function of shear stress and shear rate for a 1.0% by weight solution of cetyltrimethylammonium bromide (CTAB) and sodium salicylate in D₂O. We have also completed some preliminary measurements on the structure of a gelling colloidal silica system subjected to a shear, and related the structure changes to variations in the stress and viscosity. The combined scattering/rheometric apparatus will be a valuable resource to manipulate and characterize systems prepared under a shear or stress, or influenced by a shear or stress. Industrial examples include polymer blends, gels, and oil well drilling muds.

Publications:

Straty, G.C., Muzny, C.D., Butler, B.D., Lin, M.Y., Slawewski, T.M., Glinka, C.J., and Hanley, H.J.M., **"A Rheometric Shearing Apparatus at the NIST Center for Neutron Research (NCNR),"** Nucl. Instr. Ind. Methods in Phys. Res. (in press).

Straty, G.C., Muzny, C.D., Butler, B.D., Lin, M.Y., Slawewski, T.M., Glinka, C.J., and Hanley, H.J.M., **"An in situ Rheometric Shearing Apparatus for SANS,"** Physica B (in press).

Lin, M.Y., Hanley, H.J.M., Muzny, C.D., and Straty, G.C., **"Simultaneous Measurements of Viscosity and Structure for Rod-Like Micelles,"** Physica B (in press).

Hanley, H.J.M., **"Structure of Macromolecular Systems Under Shear; Application of Neutron Scattering,"** Colloid & Interface Sci. (in press).

22. *Surface Adsorption and Surface Structure of Surfactant/Clay Complexes*

H.J.M. Hanley, B.D. Butler, C.D. Muzny, G.C. Straty, M.Y. Lin and D.G. Peiffer (*Exxon Research and Engineering*), and **S.K. Sinha** (*Argonne National laboratory*)

Objective: To investigate the formation and structure of complexes formed by the adsorption of an organic macromolecule on an inorganic substrate and, in particular, complexes of surfactants with clay minerals.

Problem: Clay technology impacts such technologies as pollution prevention and remediation, enhanced oil recovery and the treatment of petroleum liquids, the manufacture of cosmetics and pharmaceuticals, and the synthesis of nanocomposites. These technologies involve the formation of clay/organic complexes, the properties of which are dominated by the nature of the clay-organic interfacial layer. Structural information, however, on the interfacial layer is relatively scarce.

Approach: Our work applies dynamic light scattering (DLS) and small-angle neutron scattering (SANS) to help elucidate the structure of the interface and of the complex itself. We work with particulate complexes prepared by adding a cationic surfactant to dilute aqueous suspensions of a clay mineral. DLS experiments are performed in our Boulder laboratory and are used to measure the scattered light intensity autocorrelation function at fixed scattering angle. Analysis of this function can provide an estimate of the effective hydrodynamic size of particles in a suspension and, in principle, their size distribution. SANS experiments are carried out using the small angle spectrometers at the NIST Center for Neutron Research, Gaithersburg. The SANS technique can also be used to obtain an estimate of the particle size and, in addition, an estimate of shape. Furthermore, SANS is a convenient technique to investigate micelles in the solutions.

Results and Future Plans: We have investigated aqueous mixtures of the synthetic clay mineral laponite and cetyltrimethylammonium bromide (CTAB) in dilute suspension. We found that the

SANS intensity pattern from the suspension of the pure clay is consistent with that from discs or platelets with diameters of about 30 nm. After addition of CTAB to the clay suspensions, CTAB adsorbs on the face of the clay platelets by cationic exchange and the resulting complex contains excess CTAB in an amount corresponding to about four multiples of the clay's cation exchange capacity (CEC). The analysis of the DLS data suggested two possible stable clay platelet configurations in the suspensions: (1) free clay platelets, and (2) clay platelets with CTAB adsorbed in an amount above the CEC, but presumably enough to form a stable surfactant bilayer. Plans are to investigate the solubility of the complexes in water and to model the thermodynamics of the interfacial and solubility phenomena.

Publications:

Lin, M.Y., Hanley, H.J.M., Sinha, S.K., Straty, G.C., Peiffer, D.G., and Kim, M.W., **"Shear-Induced Behavior in a Solution of Cylindrical Micelles,"** Phys. Rev E 53, R4302-R4305 (1996).

Hanley, H.J.M., Muzny, C.D., and Butler, B.D., **"Surfactant Adsorption on a Clay Mineral: Application of Radiation Scattering,"** Langmuir (in press).

Hanley, H.J.M., Muzny, C.D., and Butler, B.D., **"Surface Adsorption in a Surfactant/Clay Mineral Solution,"** Int. J. Thermophys. (in press).

Lin, M.Y., Hanley, H.J.M., Muzny, C.D., and Straty, G.C., **"Simultaneous Measurements of Viscosity and Structure for Rod-Like Micelles,"** Physica B (in press).

23. *Measurement of the Viscosity of Xenon in Microgravity*

R.F. Berg, M.R. Moldover, and G.A. Zimmerli
(NYMA, Inc.)

Objective: To test the theory for the viscosity of a fluid closer to the liquid-vapor critical point than is possible in earth's gravity.

Problem: Near the liquid-vapor critical point, theory predicts that the viscosity increases as an inverse power-law of the temperature difference from critical temperature. The increase is due to the fluid's microscopic fluctuations and it is thought to be universal for all fluids. Near the critical temperature and density, fluids on earth stratify in gravity and the predicted viscosity increase is hidden. Thus, careful tests of the theory are impossible on earth.

Approach: We measured the viscosity near the critical point of xenon onboard the Space Shuttle, where the typical acceleration is one millionth of the earth's gravity. During the ten years preceding this measurement, we established the limits on shear rate, frequency, and temperature control required to test the theory, and we developed instruments that met these limits. Only then, was a prototype viscometer built for operation on the Space Shuttle. The prototype's development led to new understanding in diverse areas, including hydrodynamic similarity, anelasticity in solids, and internal waves in stratified fluids. It culminated in detailed and realistic science requirements for the flight experiment. NASA translated these science requirements into an engineering plan, and in collaboration with NIST, developed the flight instrument on time and under budget.

In experiments on earth, NIST showed that the novel "fly-swatter" flight instrument was capable of measuring viscosity with an uncertainty of 0.2% while operating at very low frequencies and shear rates. Additional studies indicated that the instrument was robust enough to survive the stresses of launch and that vibrations typical of those on the orbiting Space Shuttle would not compromise its accuracy. Xenon was chosen as the test fluid because its other critical properties have been well measured and because of its convenient critical

temperature. The viscometer was installed into a thermostat capable of keeping the xenon sample's temperature homogeneous to within one part per billion.

Results and Future Plans: During August 1997, the Critical Viscosity of Xenon (CVX) experiment flew as part of the 11-day STS-85 Space Shuttle mission. Data from CVX were relayed to the NIST investigators at Goddard Space Flight Center for preliminary analysis. Commands were returned to CVX to optimize its performance. In microgravity, the viscosity increase was twice as large as in the best measurements on earth. The xenon's temperature was scanned through the critical temperature at rates as low as 2 K/yr. Within 1 mK of the critical temperature, the critical fluctuations caused the xenon to become viscoelastic, resulting in frequency-dependent data that could not be obtained on earth. During the next year, the analysis of the data will be completed and the results will be compared with theory.

Publications:

Berg, R.F., Zimmerli, G.A., and Moldover, M.R., "Measurement of Microkelvin Temperature Differences in a Critical Point Thermostat", Int. J. Thermophysics (in press).

24. *Hydrogen Bonding in Water at Elevated Temperatures*

R.D. Mountain

Objective: To examine the temperature and density variation of hydrogen bonding in water for states ranging from ambient to supercritical conditions.

Problem: Hydrogen bonding makes the properties of water quite different from those of most liquids. One of the current, unresolved issues in the development of a description of water at supercritical conditions is the amount of hydrogen bonding present. Different experimental probes, neutron scattering and chemical shift measurements, provide conflicting answers.

Approach: An extensive set of molecular dynamics simulations of water have been performed to develop a coherent set of hydrogen bond determinations using a model that is known to provide an accurate representation of the liquid-vapor coexistence curve, including the critical point at $T_c = 647$ K and $\rho_c = 322$ kg/m³. The temperature and density variation of the mean number of hydrogen bonds, the lifetimes of the bonds, and the degree of connectivity of hydrogen bonded molecules have been determined.

Results and Future Plans: Simulation results have been obtained for "liquid" water for temperatures between 273 K and 823 K and for densities between 1000 kg/m³ and 300 kg/m³. There are several changes in the degree of hydrogen bonding that take places in this part of the phase diagram. The first change is that as the temperature is increased from 273 K to 400 K, the lifetime of hydrogen bonds decreases from several picoseconds to about 1 picosecond and the four-fold coordination of near neighbor hydrogen bonded molecules breaks down.

A second change occurs as the density decreases from 700 kg/m³ to 500 kg/m³. In this region the connectivity of hydrogen bonded neighbors changes from a fully percolated structure to a collection of isolated, hydrogen-bonded clusters. The third change occurs at slightly supercritical temperatures, that is $T \sim 673$ K with densities lower than 600 kg/m³. Here we find physical clusters and corresponding voids with lifetimes on the order of 1 ps and sizes comparable to a few molecular

diameters. The size and lifetime distributions of the above mentioned clusters and voids will be examined further using simulations and Voronoi cell analysis. These objects are significant for theories of processes in supercritical fluids as the voids can accommodate normally insoluble molecules.

Publications:

Mountain, R.D., "**Molecular Dynamics and Hydrogen Bonds in Water,**" NIST Internal Report 6028 (1997).

Mountain, R.D., "**Molecular Dynamics and Hydrogen Bonds in Water,**" Proc. International Conference on High Pressure Science and Technology (in press).

25. *Molecular Theory of Solid-Fluid Equilibrium*

J.C. Rainwater, P.D. Beale (Univ. Colorado), S.G. Gay (Univ. Colorado), and D.G. Friend

Objective: To develop a theory of solid-fluid equilibrium for pure systems and mixtures, including hydrocarbons, refrigerants, and other compounds of industrial interest.

Problem: The complete thermodynamic description of a pure fluid or fluid mixture requires knowledge of the fluid-solid boundary. Mixtures can have a variety of interesting phase diagrams, including miscible solids, single eutectics, and solid compounds with multiple eutectics. Also of interest are the solubility of solids in liquids and supercritical fluids, the crystal structure of the solid, the heat of fusion, and the volume change on freezing.

Approach: We follow the approach of P.A. Monson and co-workers of the University of Massachusetts. The solid is described by the cell model of Lennard-Jones and Devonshire, in which the free volume is calculated for a single molecule in a cage of fixed neighboring molecules within a specified lattice structure. The molecule is initially modeled as an assembly of hard spheres, and subsequently van der Waals attractive terms and quadrupole or dipole moments are added as perturbations. The liquid free energy is obtained from a simulation, and the phase boundary is determined by a double-tangent construction. This approach can be extended to more complex molecules with arbitrary geometries and multipolar interactions.

Results and Future Plans: Starting from Monson's calculations of hard homonuclear dumbbells with quadrupole moments, we have similarly studied hard heteronuclear dumbbells with dipole moments. Our first specific candidate system has been methyl chloride, which is known to freeze into an ordered crystal. We have studied the freezing of heteronuclear hard dumbbells themselves, and have mapped out a phase diagram as a function of bond length and diameter ratio. We have studied both the lattice formed at close packing and the (different) experimental lattice. It was found that, with or

without van der Waals attraction and a dipole perturbation, the former lattice has a freezing transition but at a lower temperature than that of experiment. The experimental lattice has no freezing transition unless a dipole interaction is considered, and the dipole stabilizes a transition very close to the experimentally measured temperature. We also have investigated the possibility of simplifying the free volume calculation for the cell model. Present methods require a 5-dimensional Monte Carlo integral, but we have shown that the three spatial integrations can be done analytically, leaving two angular variables to integrate over by quadrature.

Upon completion of our calculations for methyl chloride, we plan to model methyl fluoride and carbon monoxide as systems of dipolar heteronuclear hard dumbbell molecules. Both systems are known to freeze into plastic rather than ordered crystals. We then plan to model isobutane as an assembly of four spheres and to calculate its much lower freezing temperature relative to normal butane. Subsequently, we plan to study a variety of molecules of three and four atoms modeled as assemblies of hard spheres of differing radii with moments as appropriate. We are also studying some fundamental approaches as alternatives to the cell model, and will continue to develop analytic spatial integration methods.

Publications:

Rainwater, J.C., "The Cell Model of Solid-Liquid Equilibria in Two and Three Dimensions: Analytic Spatial Free Volume Integration," *Int. J. Thermophys.* (in press).

Gay, S.C., Beale, P.D., and Rainwater, J.C., "Solid-Fluid Phase Coexistence of Hard Heteronuclear Dumbbells via Cell Theory and Monte Carlo Simulation," *Int. J. Thermophys.* (in press).

26. *Primary Acoustic Thermometry at High Temperatures*

D. Ripple (Process Measurements Division), M.R.. Moldover, and K.A. Gillis

Objectives: (1) To reduce the uncertainty in the determination of the thermodynamic temperature by a factor of 3-8 in the range from 500 K to 900 K using speed-of-sound measurements in low density argon as a primary standard, and (2) to improve the accuracy of the high-temperature fixed points (e.g. tin point, zinc point) and radiometry tied to these fixed points.

Problem: The most accurate determinations of thermodynamic temperature above 700 K use relative radiance measurements referenced to a black body near 700 K. The thermodynamic temperature of the black body is known from NIST constant volume gas thermometry (CVGT) experiments. Unfortunately, two NIST CVGT experiments differ from each other for reasons that are not well understood. The difference leads to an estimated uncertainty of 13 mK in temperatures near 700 K and 50 mK in temperatures near the gold point (1337.33 K).

Approach: We shall measure the frequencies of both acoustic and microwave resonances in a spherical, argon-filled cavity bounded by a thick, metal shell which in turn will be enclosed by a high-performance thermostat. The data will determine the speed of sound in the argon from which the thermodynamic temperature will be deduced. The temperature will be transferred to platinum resistance thermometers and then to fixed-point devices. For acoustic thermometry, the measured quantities are frequencies and the temperature. This contrasts with CVGT, which requires the measurement of pressures and temperature; thus, systematic effects will be very different in the present work and may resolve the discrepancies in the CVGT.

Results and Future Plans: A significant technical challenge was to develop electro-acoustic transducers that are compatible with the high temperatures and which neither contaminate the argon nor significantly perturb the resonance frequencies. During FY97, the resonator was

reworked and transducers were installed. The pressure vessel and furnace were fabricated and assembled.

During the next year, the resonator will be installed in the furnace. Both acoustic and microwave resonances will be measured. The flowing-gas concept will be tested and optimized. The acoustic transducers will be characterized at high temperatures.

27. *Advanced Refrigeration Systems for Cryogenic Applications*

R. Radebaugh, P. Bradley, E. Marquardt, M. Lewis, T. Kuriyama (Toshiba), J.H. Xiao (Chinese Academy of Sciences), J. Braun (Purdue Univ.), M. Hill (Univ. Colorado), and J. Gary and A. O'Gallagher (Applied and Computational Mathematics Division).

Objective: To develop new refrigeration techniques and improved refrigerator components for the temperature range of 120 K and below and to investigate and use measurement and modeling techniques for evaluating the performance of cryocoolers and their components, such as heat exchangers.

Problem: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics and magnets, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, and the liquefaction of natural gas for clean-burning transportation fuel. The use of these and other technologies has been hampered because of problems with existing cryocoolers, such as short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas.

Approach: Precision moving parts in existing cryocoolers are a source of wear, vibration, and high cost. Our approach in the development of improved refrigeration processes has been to eliminate most or all moving parts while still maintaining high efficiency. We have focused much of our research on pulse tube refrigerators, which have no cold moving parts and on the ThermoAcoustically Driven Orifice Pulse Tube Refrigerator (TADOPTR), which has no moving parts in the entire system and is a joint invention of NIST and Los Alamos National Laboratory. Our studies encompass measurements and modeling of generic losses to further improve efficiencies of these cryocoolers while increasing their lifetimes and simplifying construction techniques. NIST research in this area has much industry and other government agency support to aid in the transfer of this technology to industry.

Results and Future Plans: During the past year, measurements were made of the thermal conductance of stacked stainless steel and phosphor bronze screens of several mesh sizes and porosities at various helium filling pressures. It was found that the helium gas between the stacked screens enhanced the heat conduction through the screens by several orders of magnitude compared to vacuum. The thermal conductance degradation factors were found to be 0.1 for stainless steel and 0.022 for phosphor bronze, where this factor is the ratio of the conductance through the stacked screens to that of a solid rod of the same length and total metal cross-sectional area as the screen. Almost no prior data existed for these stacked materials, but they are needed for the optimum design of regenerative heat exchangers in many types of cryocoolers, including the pulse tube refrigerator. Packed spheres will be studied in the future.

Under a CRADA with Cryenco, Inc. of Denver, we have collaborated on a redesign of a large TADOPTR for liquefying natural gas. This is the world's largest pulse tube refrigerator and has no moving parts. The new prototype has successfully liquefied natural gas at the rate of 400 L/day. Future work will involve increasing the capacity up to about 2000 L/day. Under a CRADA with Lockheed Martin of Denver, we have also measured the performance of the world's smallest pulse tube refrigerator designed for flight on the Space Shuttle in April 1998. The effect of orifice size on the lowest temperature has been measured. The system will be delivered to NASA in January 1998 for incorporation into the Shuttle.

Publication:

Lewis, M.A., Kuriyama, T., Kuriyama, F., and Radebaugh, R., "Measurement of Heat Conduction Through Stacked Screens," *Adv. Cryo. Eng.* 43 (in press).

28. *Microscale Heat Transfer*

R. Radebaugh, E. Marquardt, M. Lewis, J.H. Xiao (*Chinese Academy of Sciences*), **M. Hill** (*Univ. Colorado*), and **J. Siegwarth**

Objective: To develop models and correlations for predicting heat transfer between fluids and solids for cases where the length or time dimensions are very small and to perform measurements to validate and improve these models and correlations.

Problem: The miniaturization of many devices such as electronics, medical probes, laser diodes, cryocoolers, etc., is hampered by the difficulty in removing heat from very small dimensions or during very short times. In most cases the heat must be transferred from a solid to some fluid. Often the fluid serves to carry the heat to another location where the heat can be dissipated over a larger region to the environment. Our knowledge of the mechanisms for heat transfer in very small dimensions is limited, and, as a result, it is difficult to properly design a device for adequate heat transfer that will not lead to overheating. In the case of oscillating heat transfer, such as in many types of cryocoolers, the system size can be miniaturized by utilizing high frequency oscillations. Difficulties in transferring heat in very short time scales limit the operating frequency and, hence, the size reduction that can be achieved.

Approach: The early stages of this program involve a review of the literature on microscale heat transfer to determine prior efforts and to find where there are the largest gaps in our ability to predict heat transfer in very small length or time scales. The scale sizes of importance to our study are in the region where the more conventional bulk or steady-state heat transfer calculations and correlations can no longer be used with any accuracy. In the case of short time scales, we are extending our prior work on regenerative cryocoolers to investigate the effect of frequency on heat transfer and pressure drop in regenerators where helium gas is the working fluid. A normalized frequency parameter, known as the dynamic Reynolds number or the Valensi number, will be used to study correlations of heat transfer and pressure drop with frequency. Existing models will be studied to verify their applicability for these cryocooler applications. In the case of heat transfer

in small length scales, we are most interested in understanding the limitations to increased heat transfer density. The systems to be studied are single- and two-phase heat transfer to allow a comparison between the two mechanisms. Multicomponent fluids are also to be studied because of their ability to be in two phases over a wide temperature range, thereby enhancing heat transfer in a heat exchanger that spans a wide temperature range.

Results and Future Plans: During the past year a literature search was carried out to gain a knowledge of previous work in the area of heat transfer to fluids in small length scales. Much of the prior work has involved the use of microgrooves in silicon surfaces. The smallest dimension of these microgrooves has usually been in the range of 200 to 500 μm . A limited number of single- and two-phase heat transfer studies has been made, but no conclusions can be drawn regarding the optimum designs of heat exchangers for the maximum heat transfer density. One study showed subcooling had no effect on the critical heat flux in two-phase heat transfer. Another study investigated the effect of fluid velocity, liquid sub-cooling, fluid properties, and micro-channel geometry on single-phase heat transfer. One study that compared single- and two-phase heat transfer gave heat transfer coefficients of about 4 to 6 $\text{kW}/(\text{m}^2 \cdot \text{K})$ for single-phase and about 12 $\text{kW}/(\text{m}^2 \cdot \text{K})$ for two-phase. Our investigation of the literature indicates that there is much work needed to even begin to understand microscale heat transfer. Future plans include the design of experiments to measure single- and two-phase heat transfer in very small dimensions. The influence of high velocities, such as jet impingement, on heat transfer will be considered for the design of such experiments.

29. *The Thirteenth Symposium on Thermophysical Properties*

W.M. Haynes, R.A. Overfelt (Auburn University), G.R. Hardin, and R.A. Stevenson

Objective: *To organize an international conference on the thermophysical properties of fluids and solids.*

Purpose: The Symposium on Thermophysical Properties is a well-established series of conferences held roughly every three years since 1959. This Symposium represents the premier international conference associated with the theoretical, experimental, and applied aspects of the thermophysical properties of gases, liquids, and solids. This conference brings together leading international experts from industry, academia, and government laboratories in these areas. NIST, in conjunction with the Thermophysical Properties Committee of the ASME Heat Transfer Division, has assumed primary responsibility for organization of this conference for more than 20 years.

The Symposium consists of plenary and parallel sessions of both general and special interest. International leaders on topics of major current interest organize special sessions, comprising about 80 percent of the sessions. Invited speakers for both the plenary and parallel sessions include international experts providing lectures on the latest developments in the wide range of topics covered at this conference. The proceedings of the conference are published in major international journals.

Response: The Thirteenth Symposium on Thermophysical Properties was held in Boulder, Colorado from June 22-27, 1997. W.M. Haynes organized this conference with assistance from R.A. Overfelt of Auburn University. The conference attracted almost 600 participants from more than 35 countries with slightly more than half from countries outside the U.S. The number of participants represented an increase of more than 40% from the Twelfth Symposium.

The conference consisted of 125 sessions over 4-1/2 days with two plenary sessions. There were as many as nine parallel sessions. The final program had 584 papers, 70 percent of which dealt with fluids.

Special sessions on alternative refrigerants, aqueous systems, chemical process design, molecular simulation, structure of fluids, acoustic techniques, supercritical fluids, low gravity, natural gas systems, databases, and correlations were organized by members of the Physical and Chemical Properties Division. Other special session topics included critical behavior, optical techniques, laser photothermal techniques, wetting and interfaces, polymers and polymer solutions, subsecond thermophysics, and thin films and coatings.

Plenary session lectures were given by Prof. John M. Prausnitz of the University of California at Berkeley, Dr. Costa Tsonopoulos of Exxon Research and Engineering Co., Prof. Peter T. Cummings of the University of Tennessee and Oak Ridge National Laboratory, and Prof. Michael E. Fisher of the University of Maryland. Prof. S. Peter Kezios of the Georgia Institute of Technology gave a presentation on the history of the Symposium on Thermophysical Properties. The Thirteenth Symposium established the Touloukian Memorial Lecture with Prof. Fisher giving the first in this series. This lecture was presented at the session in which the Yeram S. Touloukian Award was presented to Dr. Ared Cezairliyan (Metallurgy Division, NIST) and to Prof. William A. Wakeham (Imperial College, London, UK) in recognition of their outstanding technical contributions to the field of thermophysical properties.

Approximately 340 manuscripts were submitted for publication in the Symposium Proceedings, which consists of special issues of the International Journal of Thermophysics and Fluid Phase Equilibria. A preprint volume of all manuscripts was prepared on CD-ROM and distributed at the conference. The same information was placed on the Symposium Website at <http://www.boulder.nist.gov/div838/symp13/>.

The Fourteenth Symposium on Thermophysical Properties to be held in Boulder, Colorado from June 25-30, 2000 will be chaired and organized by W.M. Haynes.

30. *Fourth International Conference on Chemical Kinetics*

R.E. Huie and J.W. Hudgens

Objective: To bring together leading scientists who generate and use chemical kinetic data.

Purpose: This conference is to bring together scientists from different disciplines to discover matters of common interest in chemical kinetics. Chemical kinetics is a fundamental tool for the understanding and control of complex chemical processes, both directly by providing rate data on the elementary reactions involved, and indirectly by an improved understanding of the reactivity patterns and the thermodynamics of reactive intermediates. Many reaction types and intermediates are of key importance in a number of different areas and under widely different conditions. Often, investigators in one field are unaware of studies carried out in another field that may provide useful insights. This is particularly true if different physical phases are involved.

The conference was held July 14 through July 18, 1997. Oral sessions took place in the Red Auditorium at NIST from about 9:00 am to 4:00 pm Monday through Thursday and 9:00 am to 12:30 pm on Friday. Poster sessions were held Monday, Tuesday, and Thursday from 4:20 pm to 6:30 pm at the Gaithersburg Hilton. The Conference was also served by a World-Wide-Web site, through which conferees could obtain information about the conference, register, find out about the meeting hotel and other hotels in the area, etc. The conferees were strongly encouraged to submit their abstracts in electronic form by e-mail. These abstracts were converted to HTML format and, in this way, all abstracts for the meeting were posted on the web site and available to all the conferees well in advance of the conference. The file of conference abstracts could be searched by key word or by author, and an Acrobat file was also available for downloading. The web site also had links from the oral sessions to topical posters, to better integrate the poster presentations with the oral program.

Response: Two hundred scientists registered for the Conference. There were fifty-seven oral presentations and one hundred forty poster

presentations. The book of abstracts consisted of more than 300 pages. A wide variety of subject areas were covered at the conference, including small radical kinetics, the kinetics of inorganic radicals at high temperature, reactions of unsaturated radicals, application of theory to kinetic problems, heterogeneous reactions, combustion chemistry, and environmental chemistry. The web site was intensely utilized by the conferees in advance of the meeting, which manifested itself in better communication with the conferees and allowed better preparation on their part. This heightened the success of the meeting. As a result, in the future we envision an even greater utilization of the capabilities of the World-Wide-Web in conferences such as this.

Publications:

Conference Website at

http://www.nist.gov/cstl/div838/kinet_conf/conference.html

Program and Abstracts, Fourth International Conference on Chemical Kinetics, NIST, Gaithersburg, MD.

31. *Technology Transfer in Computational Thermochemistry*

K.K. Irikura

Objective: To publicize the scope, reliability, accessibility, and economics of computational thermochemistry.

Purpose: Global competition is shrinking the timelines for industrial process scale-up (from lab to production). This has resulted in an increased reliance on computerized modeling and simulations to replace expensive, time-consuming, and hazardous experiments. Concurrently, there has been a rapid drop in the cost of computational "horsepower," allowing the development of new predictive techniques that are practical in an industrial environment. Unfortunately, the chemical engineering community is largely unaware of this impressive recent progress. This poor communication is a major hindrance to the conversion of the science into useful technology.

Approach: Encourage communication among engineers, computational scientists, and experimental scientists, building upon their common interests in thermochemistry.

Response: In cooperation with scientists from the Dow Chemical Co., we organized the first symposium on the topic of computational thermochemistry. This included a panel discussion of the needs for and applications of accurate thermochemical data, with an emphasis on prediction. The panel members represented the users of thermochemical data in areas such as chemical processing, microelectronics, academia, and the military. The four major recommendations are expected to guide work in this area. (1) A critically evaluated, consensus database of thermochemical data is needed for methods development by scientists. (2) The scientific research base should be broadened to include the accurate prediction of a wider spectrum of engineering properties such as kinetics, vapor-liquid equilibrium parameters, critical data, and the properties of molecules on surfaces. (3) Better dissemination of these techniques to the engineering and industrial community is needed, including both publicity and user-friendly software. (4) Corporate cultures should be changed to allow private (but non-

proprietary) thermochemical data to be added to public resources such as databases and estimation software. In addition to the panel discussion, the proceedings of the entire symposium are summarized in NISTIR 5973, which is publicly available on-line. The symposium was also used as the nucleus of the first book on computational thermochemistry, published by the American Chemical Society. In the future, we intend to focus on recommendations (1) and (3) and to encourage others to pursue recommendations (2) and (4).

Publications:

Irikura, K.K. and Frurip, D.J., "Summary Report: Symposium on Computational Thermochemistry [Computers in Chemistry Division, American Chemical Society (ACS), 212th National Meeting, Orlando, Florida, August 25-29, 1996]," NIST Internal Report 5973 (1997).

On-line at

<http://properties.nist.gov/div838/refdata/irikura/symposium.pdf>

Irikura, K.K. and Frurip, D.J., "Computational Thermochemistry" and "Worked Examples," in Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics; Irikura, K.K. and Frurip, D.J., Eds.; ACS Symposium Series, ACS: Washington, DC, 1997 (in press).

Irikura, K.K., "Essential Statistical Thermodynamics" and "Glossary of Common Terms and Abbreviations in Quantum Chemistry," in Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics; Irikura, K.K. and Frurip, D.J., Eds.; ACS Symposium Series, ACS: Washington, DC, 1997 (in press).